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Silicon Isotopes as a New Method of Measuring Silicate Mineral Reaction Rates at Ambient Temperature

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Abstract

Experiments of albite dissolution under ambient temperature at pH 3 and 5 demonstrated the feasibility of using ^{29}Si doping method to precisely measure silicate mineral dissolution rates. Initial solutions were doped with ^{29}Si to result in an isotopic composition of 0.04% ^{28}Si, 99.9% ^{29}Si, and 0.06% ^{30}Si, which compares with the Amelia and Evja albite with Si isotopic composition of 92.23% ^{28}Si, 4.67% ^{29}Si, and 3.10% ^{30}Si. The isotopic contrast allows the detection of dissolution of a tiny amount of albite into the aqueous solution. Experimental results show rapid increase of ^{28}Si abundance at the initial stage of fresh albite dissolution, reflecting reaction with high energy sites on the surface. Steady state dissolution rates were reached after 20-30 days at 22 ^{o}C. The evolution of ^{28}Si and ^{29}Si abundances (%) with time tightly constrains the albite dissolution rates, which are consistent with literature data. In experiments seeded with kaolinite, both albite dissolution rates and kaolinite precipitation rates were determined with a combination of Si isotopes and isotope dilution method of determining Si concentrations.

The new experiments have also verified the assumptions that are necessary for the isotope doping method to be applicable. Experimental data showed no Si isotope fractionation during albite dissolution. The ion-exchange method in sample pre-treatments does not alter Si isotopic composition or silica concentrations. The errors from neglecting isotope fractionation during secondary mineral precipitation are small on the determined albite dissolution rates when the isotope doping is overwhelming. In conclusion, we now have substantial experimental data show that the ^{29}Si doping is a new method applicable to a wide range of silicate mineral dissolution rate determinations. Particularly, our albite experimental results show promise to use isotope doping method to measure silicate dissolution rates at various saturation states and determine the rate – ΔG_r relationships.

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1. Introduction

A core process in the Earth's Critical Zone is mineral weathering and soil formation. However, it is well known that many silicate reactions at ambient temperature and circumneutral pH are difficult to measure because Si elemental concentration changes at successive time steps are too small to be measured accurately. This situation is exacerbated near equilibrium where reaction rates are even slower. Furthermore, experimental data are hard to interpret when secondary minerals precipitate.

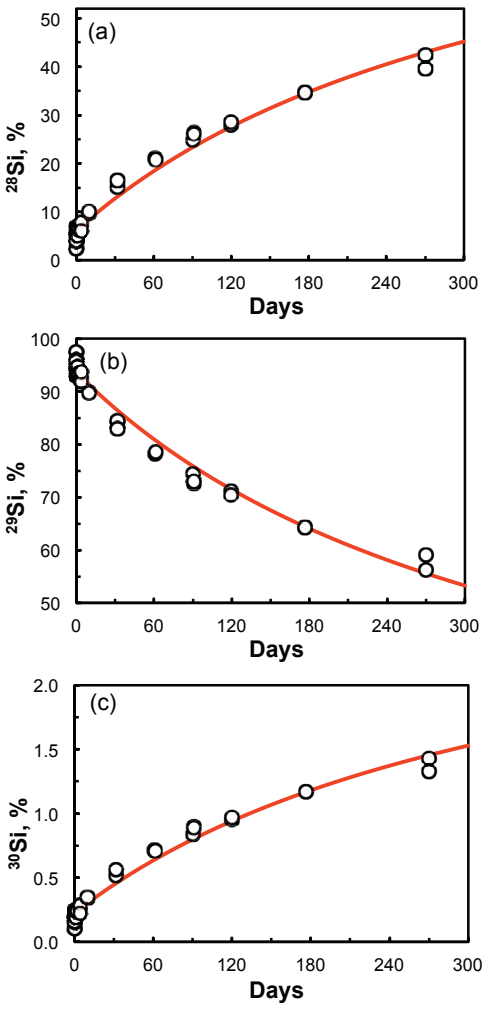

Fig 1. Si isotope abundances in aqueous solutions in batch experiments of albite dissolution at 22 °C and pH 3. The symbols are HR-MC-ICP-MS measurements. Red line denotes predictions with an albite dissolution rate of $10^{-11.75}$ mol m^{-2} s^{-1}.

To overcome these obstacles, we have developed an innovative "isotope doping method". The Amelia albite has an isotopic composition of 92.23% ^{28}Si, 4.67% ^{29}Si, and 3.10% ^{30}Si. We "doped" the initial experimental solution to resulting in a composition of 0.04% ^{28}Si, 99.9% ^{29}Si, and 0.06% ^{30}Si. See **Table 1.**

Table 1. Isotopic doping experiment conditions

	^{28}Si	^{29}Si	^{30}Si
albite	92.23%	4.67%	3.10%
Initial Solution	0.04%	99.9%	0.06%

2. Experimental results

Figure 1 shows the temporal evolution of ^{29}Si, ^{28}Si and ^{30}Si abundances in batch experiments of Amelia albite hydrolysis at pH 3 and 22 °C. The "doped" initial solution has a ^{29}Si abundance of almost 100%. Dissolution of a tiny amount of albite with 92.23% ^{28}Si resulted in a rapid decrease of ^{29}Si and an increase of ^{28}Si and ^{30}Si. At the initial stage of fresh albite dissolution, ^{28}Si abundance rapidly increased, reflecting reaction with high energy sites on the surface. The changes in ^{29}Si and ^{28}Si abundances per day far exceeded the analytical uncertainties of 0.05~0.1%.

The isotopic abundances can be fitted with a constant rate of $10^{-11.75}$ mol m^{-2} (BET) s^{-1} after four days, all the way to 270 days, the end of the experiment. Note that the fit is quite tight. In other words, the Si isotope abundance data *alone* constrained the albite dissolution rate to the second digit after decimal point in the log form ($10^{-11.75}$ mol m^{-2} (BET) s^{-1}). This value of albite dissolution rate at 22° C and pH 3 is within a wide range of previous experimental results. However, our experiments are long (up to 270 days) comparing to previous results [2].

Similar experiments at pH 5 also demonstrated the viability of the isotope doping method. Albite dissolution

rates stabilized after 20-30 days (Fig. 2). Our long-term experiments are on the slower side and are in agreement with Knauss and Wolery who used conventional method measuring Si elemental concentrations [1].

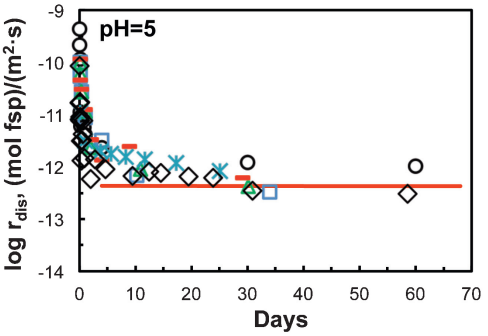

Fig 2. Albite dissolution rates at 22 °C pH 5 with different initial ^{29}Si concentrations. The symbol * stands for rates measured by Knauss and Wolery [1] with conventional method.

3. Coupled dissolution and precipitation reactions

The Si isotopes also allow us to use **the isotope dilution (ID) method** to accurately measure Si elemental concentrations. Combining the isotopic ratios and elemental Si concentration data gave the rate of secondary mineral (e.g., kaolinite, imogolite or allophone) precipitation. In other words, the isotope doping method now allows determining albite dissolution and kaolinite precipitation rates simultaneously. Zhu and co-workers had advocated that coupled reactions hold keys to resolving the apparent discrepancy between field and lab rates [3-8]. Now stable isotopes allows us explore the coupling between dissolution and precipitation reactions.

Figure 3 below shows an experiment of albite dissolution at pH 5 with kaolinite seeds. The silicon elemental concentrations calculated from isotope mixing [9], assuming no secondary mineral precipitation, are systematically higher than the silicon concentrations directly determined from the Isotope Dilution method. Assuming no secondary mineral precipitation (red line in Fig 3) would not fit either the Si or Al elemental concentration data. Kaolinite precipitation at a rate of 3 x 10^{-13} mol s^{-1} L^{-1}, although not verified mineralogically, fit both the Si and Al concentrations well.

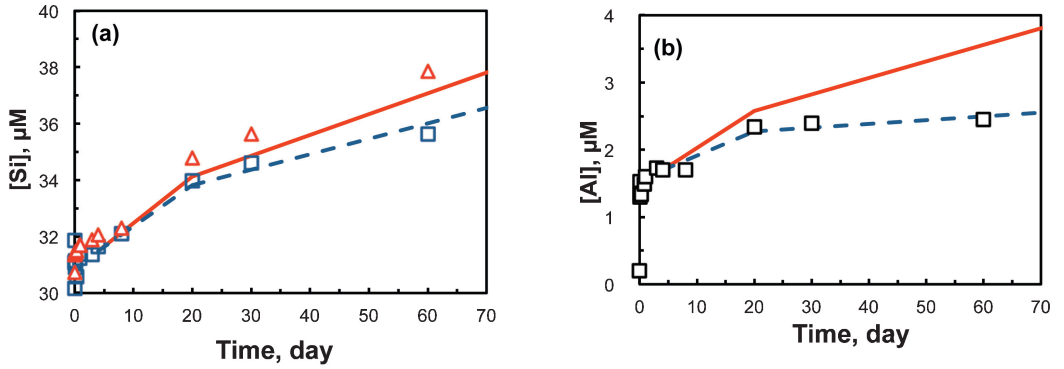

Fig 3. Albite dissolution experiments at 22 °C pH 5 with kaolinite seeds. (a) Si elemental concentrations calculated from isotopic ratios (red triangle) and from Isotope Dilution method (ID, blue squares). (b) Measured Al elemental concentrations. The red lines are modelling results assuming albite dissolution only and no secondary mineral precipitation. The blue lines assume simultaneous albite dissolution and kaolinite precipitation.

4. Experimental verification of assumptions

Additionally, for the isotope doping method to be applicable, a number of fundamental assumptions [9] have to be verified. We performed a series of experiments that are necessary for the new experimental method to be applicable:

(1) We measured Si isotopes as a function of time when no isotope doping was performed. Data showed no fractionation during albite dissolution;

(2) Ion-exchange method in sample pre-treatments [10] does not alter Si isotopic composition or silica

concentrations; and

(3) The errors from neglecting isotope fractionation during secondary mineral precipitation are small on the determined albite dissolution rates when the isotope doping is overwhelming.

5. Conclusions and remarks

Substantial amount of experimental data are now available and have demonstrated that the silicon isotope doping method works well in determining silicate dissolution rates at ambient temperature and in determining coupled dissolution and precipitation rates. The experimental data on albite also showed the following potentials of this method, which can be further explored. **Fig 2** shows that Si isotope data captured the initial rapid dissolution of highly reactive surface sites. This information is not available from Si elementary analysis. However, these data show that Si isotopes can be utilized as a "probe" to answer some nagging questions of "reactive surface area"[11]. The stabilized albite dissolution rates showed dependence on the saturation with respect to albite. The rate – ΔGr relationships are controversial in the geochemistry community [12-14], on "Burch-type rate law" versus transition state rate laws. Therefore, our albite experimental results show promise to use isotope doping method to measure silicate dissolution rates at various saturation states and determine the rate – ΔGr relationships.

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